

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 376 447
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89311214.4

(61) Int. Cl.⁵: C25C 7/02, C25D 17/10

(22) Date of filing: 31.10.89

The title of the invention has been amended
(Guidelines for Examination in the EPO, A-III,
7.3).

(30) Priority: 31.10.88 ZA 888151

(43) Date of publication of application:
04.07.90 Bulletin 90/27

(84) Designated Contracting States:
DE ES FR GB NL

(71) Applicant: ZIMCO INDUSTRIES
(PROPRIETARY) LIMITED
5th Floor
Sandton City Sandton Transvaal(ZA)

(72) Inventor: Thom, Michael John
Tangmere Farm Bushyvaies
South Coast Natal(ZA)

(74) Representative: White, Martin David
MARKS & CLERK 57/60 Lincoln's Inn Fields
London WC2A 3LS(GB)

(54) Electrode for electrochemical use.

(57) An anode which includes a body (14) which is made principally of lead or of aluminium with a 20 micron coating (22) of an alloy of 95% lead, 5% silver on the body.

The anode reduces lead ion migration through an electrolyte to a cathode during the electrowinning of zinc.

EP 0 376 447 A1

BACKGROUND OF THE INVENTION

This invention relates generally to an electrode and more particularly is concerned with an electrode of the type used as an anode in, for example, the electrowinning of zinc.

Pure lead anodes have been used for electrolyzing zinc from an aqueous solution of zinc sulphate in diluted sulphuric acid on to an aluminium or zinc cathode. However, with a pure lead anode, lead ions migrate to the cathode and reduce the purity of the zinc which is recovered in the process.

Silver has been added to the lead anode to reduce the aforementioned problem of lead ion migration. The addition of silver, of from 0.5% to 1% by weight to the anode, does reduce lead ion migration and at the same time hardens the anode slightly thereby increasing its resistance to corrosion and increasing its life. Obviously an anode of this type costs more due to the expense of the silver.

SUMMARY OF THE INVENTION

The invention is concerned with an electrode in which the amount of silver, or equivalent additive, is reduced.

The invention provides an electrode which includes an electrode body and at least one coating of a lead alloy on at least a portion of the electrode body.

The lead alloy used for the coating may comprise a lead/silver alloy, a lead/palladium alloy, or a lead/silver/palladium alloy.

A plurality of the lead alloy coatings may be formed on the body, each with different properties.

The lead alloy may contain from about 90% to 97% lead by weight. A suitable lead content is of the order of 95% with the remainder, 5%, being silver, palladium or a mixture of silver and palladium.

The lead alloy coating may have a thickness of from 1 to 100 microns and preferably the thickness of the coating is from 10 to 20 microns.

The lead alloy coating may have formed on it a layer of lead dioxide, lead peroxide or manganese dioxide. This, in a manner which is not fully understood, provides a protective coating to the electrode which reduces lead loss from the anode surface and thereby improves the quality of zinc recovered in an electrowinning process.

In one form of the invention the electrode body is made at least principally of lead and preferably comprises lead alloyed with at least one of the following: calcium, barium and strontium.

In another form of the invention the electrode body is made at least principally from aluminium. To improve the adherence of the lead alloy coating to the electrode body an undercoat of a silver or gold layer, or equivalent, may be provided on the aluminium electrode body and the lead alloy coating may be formed thereon.

Aluminium is lighter than lead and is a far better conductor of electricity and consequently it is possible to form an aluminium based electrode with the same surface area as a lead based electrode, but thinner.

The silver or gold undercoat may have a thickness which is less than 1 micron and for example may be of the order of 0.5 microns thick.

The invention also provides a method of forming an electrode which includes the step of forming at least one coating of a lead alloy on an electrode body.

The lead alloy may comprise one of the following: a lead/silver alloy, a lead/palladium alloy, and a lead/silver/palladium alloy.

The lead alloy may contain from 90% to 97% lead by weight and preferably contains lead in the amount of approximately 95%.

The lead alloy coating may have a thickness of from 1 to 100 microns and preferably the thickness is of the order of from 10 to 20 microns.

The lead alloy may be electrodeposited on the electrode body in an electrolysis tank and the electrolyte in the tank may comprise a lead hydroxide and silver cyanide solution, in the presence of sodium cyanide and sodium hydroxide, or of potassium cyanide and potassium hydroxide, or a mixture thereof.

The method may include the step, prior to forming the lead alloy coating, of preparing the surface of the electrode body by means of at least one process selected from the following: sandblasting, electropolishing and exposure to a suitable reagent such as a dilute acetic or nitric acid solution.

The surface of the electrode body may be etched, ridged, pitted, oxidised, activated or passivated to receive a stable and uniform coating thereon.

One or more layers of the lead alloy coating may be applied to the electrode body. Each coating may be of the same or a different composition.

In one form of the invention the electrode body is made from lead alloyed with at least one of the following: calcium, barium and strontium.

In a different form of the invention the electrode body is made from aluminium with a silver or gold undercoat on which the lead alloy coating is

formed. It is possible to form the lead alloy coating on the electrode body by first tinning or soldering the electrode body in an inert atmosphere with a suitable tin/lead alloy, or by applying the alloy using a flux. The tin/lead alloy prevents the surface of the aluminium electrode body, once cleaned, from oxidising, and provides a substrate for the lead coating.

The principles of the invention are particularly suitable for producing an anode for use in the electrowinning of zinc. The invention is thus intended to cover an electrolysis cell for the electrowinning of zinc which includes an aqueous solution of zinc sulphate in diluted sulphuric acid, a cathode which is made at least principally from aluminium or zinc, and an anode of the aforementioned kind.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of examples with reference to the accompanying drawings in which:

Figure 1 schematically depicts the production of an anode in accordance with the principles of the invention.

Figure 2 is a cross sectional view of portion of an anode according to one form of the invention.

Figure 3 schematically depicts the use of the anode of the invention in the electrowinning of zinc, and

Figure 4 shows a modification to the arrangement of Figure 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 1 illustrates an electrolysis tank 10 which contains an electrolyte 12 of lead hydroxide and silver cyanide solution, in the presence of sodium cyanide and sodium hydroxide, or of potassium cyanide and potassium hydroxide, or a mixture thereof.

Located in the electrolyte are a plurality of anode bodies 14 which are electrically connected to one terminal of a power supply 16, and a plurality of lead sheets 18 which are electrically connected to a second terminal of the power supply 16. The power supply is under the control of a control unit 20 whereby the amplitude of the voltage, the current waveform produced by the supply 16, and the time period for which current flows from the power supply through the electrolyte 12, can be controlled. The power supply 16 and the control unit 20 are known in the art and consequently are not further described herein. It is to be noted the current in the electrolyte can also be

varied by changing the electrolyte composition, or by altering the spacings between the anode bodies 14 and the lead sheets 18.

Each anode body 14 is made, according to one embodiment of the invention, from lead which is alloyed with calcium. It is to be noted however that it is possible to alloy the lead with barium or strontium instead of or in addition to the calcium.

Prior to being placed in the electrolyte each lead anode body is cleaned by sandblasting, by electropolishing or by being dipped into a suitable reagent such as diluted acetic acid or nitric acid solution. The lead anode bodies are evenly spaced in the electrolyzing tank.

The lead sheets, in this embodiment of the invention, contain from 4% to 7% silver by weight and are placed between the anode bodies 14, again evenly spaced from one another. The silver content is chosen so that 5% silver is deposited on the anode bodies 14.

When current flows between the bodies 14 and the lead plates 18 a coating of lead and silver, from the plates 18, is electrodeposited on the anode bodies 14. By using the control unit 20 it is possible to regulate the thickness of the silver/lead coating, on the anode bodies, to from 1 to 100 microns and, preferably, to a thickness of the order of 20 microns. The lead anode body with the lead/silver coating can be coated with a thin layer of lead oxide, lead peroxide or manganese dioxide. This reduces the loss of lead from the anode when it is used in the production of zinc.

The lead plates 18 have been described as including silver. Instead of silver, or in addition thereto, palladium may be used in the coating composition. Equally beneficial results are obtained.

Figure 2 illustrates a portion of anode body 14 with a lead/silver coating 22 deposited thereon. A thin layer 24 of lead dioxide covers the coating 22.

According to a different embodiment of the invention the anode body 14 is not formed from a lead alloy but, instead, from aluminium. Aluminium is less dense than lead and is far more electrically conductive than lead and it is possible therefore to form the anode body so that it is thinner than for a lead anode body, but with the same surface area. Aluminium oxidises readily and in order to ensure that the lead alloy coating 22 adheres to the aluminium body it is necessary to clean the surface of the aluminium body in an inert atmosphere for example a nitrogen atmosphere. The aluminium body can then be coated with silver, by a chemical, electrolytic or other suitable process, in a very thin layer designated 26 in Figure 2, of the order of 0.5 microns. Thereafter the silver coated aluminium anode body can be used, in the manner described in connection with Figure 1, and have applied to it

a lead/silver coating. Again it is possible to use palladium in place of or in addition to the silver.

An anode formed in the manner described performs adequately in an electro chemical cell for the electrowinning of zinc with a reduced quantity of lead ions migrating from the anode on to the cathode which is used. This results in zinc with a high degree of purity being produced in the process.

Figure 3 schematically depicts a zinc electrowinning process wherein an anode 28, produced in accordance with the principles of the invention, in the manner which has been described hereinbefore, is located in an electrolyte 30, such as zinc sulphate in diluted sulphuric acid, in an electrolysis tank 32. A cathode 34 of aluminium or zinc is also placed in the electrolyte and the anode and the cathode are connected to a power supply 36 under the control of a control unit 38. As has been pointed out the migration of lead ions from the anode 28 to the cathode 34 is reduced. The reason for the reduction in ion migration is not fully understood but it is believed that as electrolysis is in essence a surface reaction it is possible to achieve the benefits of a lead/silver or lead/palladium anode by providing a high silver to lead content only on the surface of the anode.

It is to be noted that the silver to lead ratio in the sheets 18 is varied so that the desired proportion of silver is electrodeposited on the anode bodies 14. If the anode bodies are to have 5% of silver in their coatings then, depending on the circumstances, the lead sheets 18 may have from 4% to 7% silver.

An alternative method of controlling the silver content of the coatings is to make use of two electrodes 18A and 18B in place of a single lead sheet 18, as indicated in Figure 4 which shows a portion of the arrangement of Figure 1.

The electrode 18A may be pure lead while the electrode 18B is pure silver or 50% silver/50% lead alloy. The current through each electrode is then finely and separately controlled by means of separate power supplies 16A and 16B respectively, so that the percentage of silver, in each coating, can be accurately controlled.

Claims

1. An electrode which includes an electrode body (14) and which is characterized by at least one coating (22) of a lead alloy on at least a portion of the electrode body.

2. An electrode according to claim 1 characterized in that the lead alloy (22) is at least one of the following: a lead/silver alloy and a lead/palladium alloy.

3. An electrode according to claim 1 or 2

characterized in that the lead alloy (22) contains from 90% to 97% lead by weight.

4. An electrode according to any one of claims 1 to 3 characterized in that the lead alloy coating (22) has a thickness of from 1 to 100 microns.

5. An electrode according to claim 4 characterized in that the thickness of the lead alloy coating (22) is of the order of 20 microns.

6. An electrode according to any one of claims 1 to 5 which is characterized in that it includes, on the lead alloy coating (22), a layer of a material selected from the following: lead dioxide, lead peroxide and manganese dioxide.

7. An electrode according to any one of claims 1 to 6 characterized in that the electrode body (14) is made at least principally from lead.

8. An electrode according to claim 7 characterized in that the electrode body (14) is made from lead alloyed with at least one of the following: calcium, barium and strontium.

9. An electrode according to any one of claims 1 to 6 characterized in that the electrode body (14) is made at least principally from aluminium.

10. An electrode according to claim 9 characterized in that the aluminium electrode body (14) has an undercoat of a silver or gold layer (26) on which the lead alloy coating (22) is formed.

11. A method of forming an electrode which is characterized in that it includes the step of forming at least one coating (22) of a lead alloy on an electrode body (14).

12. A method according to claim 11 characterized in that the lead alloy (22) is at least one of the following: a lead/silver alloy and a lead/palladium alloy.

13. A method according to claim 11 or 12 characterized in that the lead alloy (22) contains from 90% to 97% lead by weight.

14. A method according to any one of claims 11 to 13 characterized in that the lead alloy coating (22) has a thickness of from 1 to 100 microns.

15. A method according to any one of claims 11 to 14 characterized in that the lead alloy (22) is electrodeposited on the electrode body (14) in an electrolysis tank (10).

16. A method according to claim 15 which is characterized in that it includes the steps of electrodepositing the lead alloy (22) on the electrode body (14) from at least two electrodes (18A and 18B) of different compositions, and of separately controlling the rate of electrodeposition from each electrode to the electrode body thereby to control the composition of the deposited lead alloy.

17. A method according to claim 15 or 16 characterized in that the electrolyte (12) in the tank (10) is a lead hydroxide and silver cyanide solution, in the presence of sodium cyanide and sodium hydroxide, or of potassium cyanide and potassium

hydroxide, or a mixture thereof.

18. A method according to any one of claims 11 to 17 which is characterized in that it includes the step, prior to forming the lead alloy coating (22), of preparing the surface of the electrode body (14) by means of at least one process selected from the following: sandblasting, electropolishing and exposure to a reagent.

19. A method according to any one of claims 11 to 18 characterized in that the electrode body (14) is made from lead alloyed with at least one of the following: calcium, barium and strontium.

20. A method according to any one of claims 11 to 18 characterized in that the electrode body (14) is made from aluminium with a silver or gold undercoat on which the lead alloy coating is formed.

5

10

15

20

25

30

35

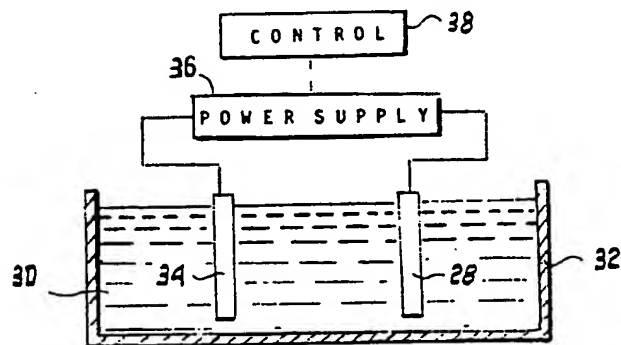
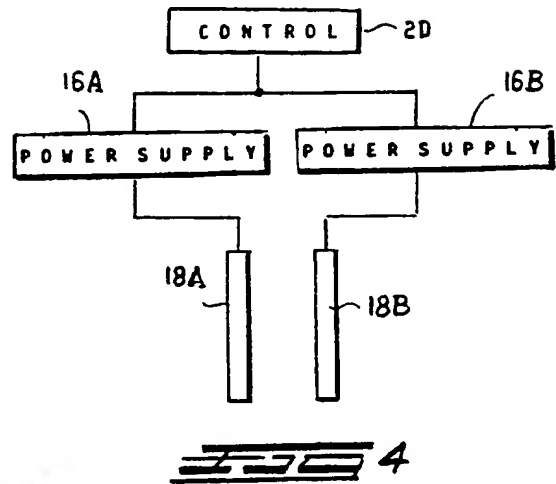
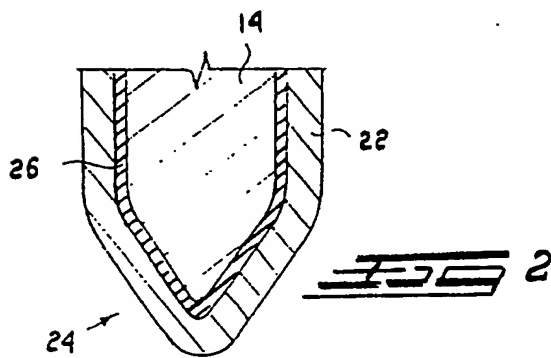
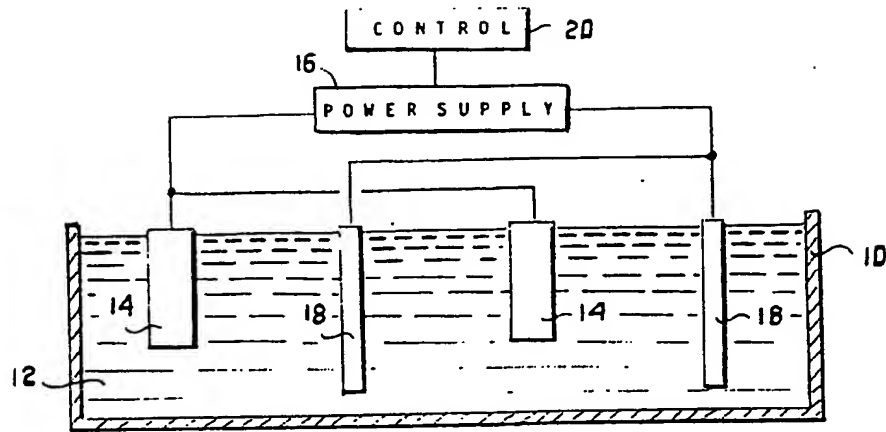
40

45

50

55

5





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 194 321 (BLEIINDUSTRIE GmbH) * Page 2, lines 1-18; pages 7-9, claims * ---	1,2,4,5 ,7,11, 12,14	C 25 C 7/02 C 25 D 17/10
X	EP-A-0 090 435 (DIAMOND SHAMROCK CORP.) * Pages 11,12, examples 1,2; page 18, claims 1,3,4,6 * ---	1,2,9, 11,12, 14,15, 18	
X	FR-A-2 399 490 (AMMI S.p.A.) * Page 10, claims * ---	1,2,9, 11,12	
A	US-A-3 392 094 (F.S. GAUNCE) * Column 1, lines 57-72; column 2, lines 1-12 * ---	6	
A	OA-A- 5 187 (B.J. KNIGHT) * Page 33, lines 14-21 * -----	8,19	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 25 C 7 C 25 D 17
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-02-1990	Examiner GROSEILLER PH.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			